

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
18 April 2002 (18.04.2002)

PCT

(10) International Publication Number
WO 02/30200 A1

(51) International Patent Classification⁷: A01N 47/40 //
(A01N 47/40, 53:08)

Christoph [DE/DE]; Neumühlstrasse 16, 65510 Hünstet-
ten-Beuerbach (DE).

(21) International Application Number: PCT/EP01/10844

(22) International Filing Date:
20 September 2001 (20.09.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
00121924.5 7 October 2000 (07.10.2000) EP

(71) Applicant (*for all designated States except US*): AVEN-
TIS CROPSCIENCE GMBH [DE/DE]; Brüningstrasse
50, 65929 Frankfurt (DE).

(81) Designated States (*national*): AE, AG, AL, AM, AU, AZ,
BA, BB, BG, BR, BY, BZ, CA, CN, CO, CR, CU, CZ, DM,
DZ, EC, EE, GD, GE, HR, HU, ID, IL, IN, IS, JP, KG, KP,
KR, KZ, LC, LK, LR, LT, LV, MA, MD, MG, MK, MN,
MX, NO, NZ, PH, PL, RO, RU, SG, SI, SK, TJ, TM, TT,
UA, US, UZ, VN, YU, ZA.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,
CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD,
TG).

Published:
— with international search report

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): KNAUF, Werner
[DE/DE]; Am Morgengraben 6, 65835 Liederbach (DE).
HUART, Gerald, Michel, Yvon [FR/FR]; 12 A, chemin
de Calabert, F-69130 Ecully (FR). GROSSER, Kay,



WO 02/30200 A1

(54) Title: PESTICIDAL COMPOSITION

(57) Abstract: Pesticidal compositions comprising deltamethrin and acetamiprid.

Pesticidal composition

This invention relates to pesticidal compositions containing acetamiprid.

In FR 2784011 there are described mixtures of pyrethroids with a chloronicotinyl insecticide, such as imidacloprid, acetamiprid or nitenpyram. The only pyrethroid specifically disclosed is cypermethrin. US-A 5,880,142 describes mixtures of chloronicotinyl insecticides and pyrethroids for termite control and discloses a mixture of acetamiprid and cyfluthrin.

We have now found that a mixture of another pyrethroid, deltamethrin, with acetamiprid has advantageous properties over the individual components and that synergism is often demonstrated.

Accordingly the present invention provides a pesticidal composition comprising

- a) deltamethrin and
- b) acetamiprid.

Deltamethrin is the common name for (S)- α -cyano-3-phenoxybenzyl (1R,3R)-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate and acetamiprid is the common name for E-N¹-[(6-chloro-3-pyridylmethyl)]-N²-cyano-N¹-methylacetamidine.

The ratios of the deltamethrin to acetamiprid vary over a wide range but are usually in the range 5:1 to 1:10, especially 1:1 to 1:5.

In addition, other pesticides may be employed in conjunction with the active ingredients described above providing they do not adversely affect the interaction between the components a) and b). For example it is sometimes useful to include additional insecticides or acaricides to extend the range of activity in order to control a wider spectrum of pests.

The combination is also useful in overcoming reduced sensitivity by a pest to either of the individual components .

The compositions of the invention are active against a wide range of pests, especially sucking pests such as Thrips spp., e.g. *T. tabaci* and *T. palmi*, Homoptera, including aphids such as *Megoura viciae* and plant hoppers, such as *Nilaparvata lugens* and *Nephotettix cincticeps*, whiteflies, such as *Trialeurodes vaporariorum* and *Bemisia tabaci*, and *Psylla* spp., Heteroptera. e.g. bed bugs such as *Cimex lectularius*, and capsids, Lepidoptera, including *Spodoptera* spp, eg *S. littoralis*, *Heliothis* spp., eg *H. armigera* and *H. virescens*, and *Pieris brassicae*; Diptera, including *Musca domestica*, *Ceratitis capitata*, *Erioischia brassicae*, *Lucilia sericata* and *Aedes aegypti*; Coleoptera, including *Phaedon cochleariae*, *Anthonomus grandis* and corn rootworms (*Diabrotica* spp. e.g. *D. undecimpunctata*); Orthoptera, including cockroaches, such as *Blattella germanica*; ticks, e.g. *Boophilus microplus*; lice, including *Damalinia bovis* and *Linognathus vituli*; as well as spider mites such as *Tetranychus urticae* and *Panonychus ulmi*.

The compositions of the invention may be employed in many forms and are often most conveniently prepared in aqueous form immediately prior to use. One method of preparing such a composition is referred to as "tank mixing" in which the ingredients in their commercially available form are mixed together by the user in a quantity of water.

In addition to tank mixing immediately prior to use the compositions containing deltamethrin and acetamiprid may be formulated into a more concentrated primary composition which is diluted with water or other diluent before use. Such compositions may comprise a surface active agent in addition to the active ingredients and examples of such compositions are as follows.

It can be a dispersible solution which comprises the active ingredients dissolved in a water-miscible solvent with the addition of a dispersing agent. Alternatively it can comprise the ingredients in the form of a finely ground powder in association with a

dispersing agent and intimately mixed with water to give a paste or cream which can if desired be added to an emulsion of oil in water to give a dispersion of active ingredients in an aqueous oil emulsion.

An emulsifiable concentrate comprises the active ingredient dissolved in a water-immiscible solvent which is formed into an emulsion with water in the presence of an emulsifying agent.

A granular solid comprises the active ingredients associated with powder diluents such as kaolin, which mixture is granulated by known methods. Alternatively it comprises the active ingredients adsorbed or absorbed on a pre-granular diluent, for example Fuller's earth, attapulgite or limestone grit.

A dispersible or wettable powder usually comprises the active ingredients in admixture with a suitable surfactant and an inert powder diluent such as china clay.

Another suitable concentrate is a flowable suspension concentrate which is formed by grinding the active ingredients with water, a wetting agent and a suspending agent.

In some circumstances it may be desirable to combine two types of formulation e.g. one of the components is present in an emulsifiable concentrate and the second components is dispersed as a powder in this concentrate.

The concentrate of the active ingredients (when used as the sole active components) in a composition for direct application to the crop by conventional ground methods is preferably within the range of 0.001 to 10 per cent by weight of the composition, especially 0.005 to 5 per cent by weight, but more concentrated compositions containing up to 40 per cent may be desirable in the case of aerial sprays.

The invention thus includes a method for controlling a pest, especially an arthropod pest, e.g. an insect pest or an Acarina pest, which comprises applying to the pest or its locus, deltamethrin and acetamiprid either together or in sequence.

Further there is provided the use of a mixture comprising deltamethrin and acetamiprid for controlling pests.

The disclosures in European patent application No. 00121924.5 from which this application claims priority, and in the abstract accompanying this application are incorporated herein by reference.

The invention is illustrated in the following Example which describe experiments in which a synergistic effect was observed. The desired concentration of the active ingredients was achieved by diluting, with water, the commercially available 25% by volume emulsifiable concentrate of deltamethrin and 20% by weight water soluble powder of acetamiprid, each of which contained conventional surfactants.

Example

Two plants of two week old French beans (*Phaseolus vulgaris*) were infested with adult whitefly (*Trialeurodes vaporariorum*) for oviposition in a closed chamber. After 48 hours, the adults were blown off the plants so that only the eggs stayed at the surface of the leaves. The plants were placed in a greenhouse for 7 days to complete the development of the eggs to the larval stage L 1/2. The plants were then sprayed with the individual compounds and mixtures of the two, by hand with a spray gun, until complete coverage of the plant surfaces with the spray liquid was obtained. The plants were then placed in the greenhouse for a further 10 days. Two replicates of each test was carried. The mortality of the nymphs of *Trialeurodes vaporariorum* was estimated 10 days after application and the average of the two replicates calculated.

To indicate the existence of synergism between the active components the results were treated in the manner described by Colby S.R., "Calculating Synergistic and

Antagonistic Responses of Herbicide Combinations" in Weeds 1967 15, 20-22). In this method the "expected" percent control, E, of the combination is given by the equation.

$$E = X + Y - \frac{XY}{100}$$

in which

X = the percentage of control with substance A at a given rate (p),

Y = the percentage of control with substance B at a given rate (q), and

E = expected control by A+B at a rate p+q.

If the observed control of the mixture is greater than E the results indicate synergism.

The results were as follows:

deltamethrin (D) (ppm)	acetamiprid (A) (ppm)	mortality in (%)	Expected mortality (E) according to Colby
1	---	73,75	
0,6	---	47,5	
0,33	---	47,5	
0,2	---	36,25	
0,1	---	25	
0,06	---	15	
0,033	---	8,75	
0,02	---	2,5	
0,01	---	0,75	
0,006	---	0	
---	3	56,25	
---	1	23,75	
---	0,3	7,5	
---	0,1	1,25	
---	0,03	0	
1	3	82,5	88,5
0,33	1	82,5	60
0,1	0,3	55	30,6
0,033	0,1	35	9,9
0,01	0,03	8,75	0,75
0,6	3	93,75	77,0
0,2	1	63,75	51,4
0,06	0,3	33,75	21,4
0,02	0,1	10,5	3,7
0,006	0,03	2,25	0

The LC_{50} in ppm of the mixtures was calculated and compared with the expected LC_{50} from the expected mortalities according to Colby.

The results were as follows:

Ratio of D:A	LC_{50} (ppm)	LC_{50} (ppm), expected according to Colby
1:3	0,261	0,631
1:5	0,523	1,000

Claims

- 1) A pesticidal composition comprising
 - a) deltamethrin, and
 - b) acetamiprid.
- 2) A composition according to claim 1 wherein the ratio of the deltamethrin to acetamiprid is in the range 5:1 to 1:10.
- 3) A method for controlling a pest, which comprises applying to the pest or its locus, deltamethrin and acetamiprid, either together or in sequence.
- 4) The use of composition according to claim 1 or 2 for controlling pests.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 01/10844

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A01N47/40 //(A01N47/40,53:08)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 880 142 A (OTSU YUICHI ET AL) 9 March 1999 (1999-03-09) Table I: (a)-2 + (b)-1	1-3
X	FR 2 784 011 A (RHONE POULENC AGROCHIMIE) 7 April 2000 (2000-04-07) cited in the application claim 2	1-3

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

B document member of the same patent family

Date of the actual completion of the international search

21 January 2002

Date of mailing of the international search report

25/01/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3018

Authorized officer

Bertrand, F

INTERNATIONAL SEARCH REPORT
Information on patent family members

In International Application No
PCT/EP 01/10844

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 5880142	A	09-03-1999	JP	8099809 A	16-04-1996
			US	5661164 A	26-08-1997
FR 2784011	A	07-04-2000	FR	2784011 A1	07-04-2000